

SYNTHESIS AND PARTICLE SIZE CHARACTERIZATION OF CdSe SEMICONDUCTOR QUANTUM DOTS

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ABSTRACT

Nanoparticles exhibit unique physical properties that are not found in their bulk counterpart. Cadmium selenid nanoparticles are synthesized with different sizes by the organometllic pyrolysis method after modification. X-ray scattering are used to determine the average size and the internal structure of the CdSe nanoparticles. The transmission electron microscopy (TEM) images of the samples show that the mean sizes of QDs are 4 nm. The effect of particle sizes on the optical properties is confirmed from UV–visible and fluorescence spectroscopic data. The CdSe nanoparticle exhibits red shift excitonic energy band at wavelength of ~500 nm to ~600 nm. The optical band gap decreases with increasing the particle size.

KEYWORDS: Cadmium Selenide Nanoparticles, Organometllic Pyrolysis Method, Electron Microscopy, X-ray Diffraction, Optical Properties

INTRODUCTION

Nanostructured materials have attracted a great transaction of attention in the last few years for their unique characteristics that cannot be obtained from conventional macroscopic materials. Owing to the quantum size effects and surface effects, nanoparticles can display novel optical, electronic, magnetic, chemical and structural properties that might find many important technological applications. An extremely active and prolific field in nanomaterials is finding ways to control size and morphology of the nanoparticles since the properties and applications of the nanoparticles are largely dependent on their size and morphology. The most evident manifestation of properties is the optical light emission in the blue–red spectral region characterized by a blue shift at smaller crystallite dimensions. Such properties construct semiconducting nanostructures suitable for several kinds of applications, from anti reflecting coatings [1] to bimolecular detection [2] and light emitting devices [3]. Due to these changes in properties with the crystallites size, researchers interest turn towards the synthesis of semiconductor particle in the few nanometer range with dimensions comparable to the Bohr radius. The semiconductor nanoparticles within the dimension of Bohr radius exhibit strong size dependent properties. Such particles may lead to quantum dot lasers, single electron transistors and also have biological applications [4, 5]. It is important to synthesize nanoparticle at the desired size within a narrow size distribution and in an easy to handle conditions of precursor, solvent and temperature etc. Cadmium selenide (CdSe) is a brilliant II–VI semiconductor material with a direct band gap of 1.77 eV at room temperature because of their size-dependent (and thus tunable) photo- and electro-luminescence properties. CdSe can have two different crystal structures cubic zinc blende and hexagonal wurtzite and a direct band structure. CdSe quantum dots of appropriate size can have an absorption edge and emission peak anywhere in the visible spectrum. This led to CdSe nanoparticles to be used for opto-electronic devices, laser diodes, nanosensing and biomedical imaging [6]. In the present study, we have developed the conventional organometallic pyrolysis method to synthesis CdSe nanoparticles with some significant advantages such as controllable particle size, a cost-effective and less complicated technique. The prepared nanoparticles are well characterized by X-ray powder

diffraction, TEM, UV-vis and fluorescence spectroscopic data. The vibrational structure and the change of the optical properties with the particle size are also discussed.

EXPERIMENT

Synthesis of CdSe Nanoparticles

The synthesis of CdSe carried out in analogies to the procedure which developed by Murray *et al* [7], with some modifications. 0.3 gm of CdO is added to 2.0 gm of Stearic acid (as reducing agent), then heated up to 170 °C till the red color of CdO disappears completely to ensure that the reaction between CdO and Stearic acid is complete and CdO completely transform to Cd stearate. 4gm of Tri-n-octyl-phosphine oxide (TOPO) as controller solvent and 2.0 gm of HAD are added to the reaction mixture then heated under Ar atmosphere at 200 °C. In another vessel 0.30 gm of Se powder is dissolved in 6 ml of TOP. The contents of the vessel are injected rapidly to a hot solution of TOPO at 220°C. The color of the reaction mixture turns orange. Increasing the temperature leads to further growth of the particles. Different sizes of CdSe quantum dots could be separated by taking 2 ml of the reaction mixture at various temperatures. Seven samples of CdSe nanocrystals are taken from the above plot of reaction mixture at different time. Once the temperature of the reaction mixture reaches at 280°C the reaction flask was removed from the heating mantel, and then allowed to cool down. The CdSe particles can be separated in solid by adding methanol to the solution until the solution become turbid. The particles will precipitate and can be separated by centrifugation.

Instruments

The shape, morphologies and the particle size were studied using JEOL JEM 2100 transmission electron microscope operated at 200 KV accelerating voltage. The structure of the prepared samples were determined from X-ray Diffractometer Philips PW 1700 powder diffractometer operating with CuK α anode ($\lambda = 0.154183\text{nm}$). Scans were done at 6°min^{-1} for 2θ values between 20 and 90°. UV-visible absorbance spectra of prepared CdSe nanoparticles were measured with a spectrometer PerkinElmer Lambda 750 double beam spectrophotometer. Diluted solutions of target samples were placed in 1 cm UV quartz and the absorption was recorded within the appropriate scan range. The spectra were taken against the pure solvent reference of concern for each different sample. Photoluminescence PL properties CdSe nanoparticles are characterized by PerkinElmer Lambda LS 45 Spectrofluorometer to carry out the emission spectra for different sizes.

RESULTS AND DISCUSIONS

X- ray Diffraction Pattern Data

Figure 1 shows the corresponding X-ray diffraction patterns of CdSe nanoparticle deposited on a silicon slide. Indexing process of powder diffraction pattern is done and Miller Indices (h k l) to each peak is assigned in first step. The details are seen in table 1. No spurious diffractions due to crystallographic impurities are found in the sample. All the reflections are corresponding to pure CdSe semiconductor with wurtzite (WZ) hexagonal structure. However, the diffraction peaks are broad which indicating that the crystallite size is very small. Seven peaks at 2θ values of 21.83, 25.51, 34.89, 42.52, 45.86, 49.97 and 55.75 which are corresponding to (100), (002), (102), (110), (103), (112) and (202) planes of wurtzite hexagonal CdSe crystal are observed and compared with the standard powder diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS), CdSe file No. 04-011-9601. The two peaks corresponding to (102) and (103) plane confirmed the wurtzite hexagonal lattice structure. The average particle size of CdSe nanoparticle was calculated from Debye-Scherrer formula [8], $D = 0.9 \lambda / \beta \cos \theta$. Where ' λ ' is wave length of X-Ray (0.1541 nm), ' β ' is

FWHM (full width at half maximum), ' θ ' is the diffraction angle and 'D' is particle diameter size. The calculated values of crystalline particle size (D) were listed in table 1.

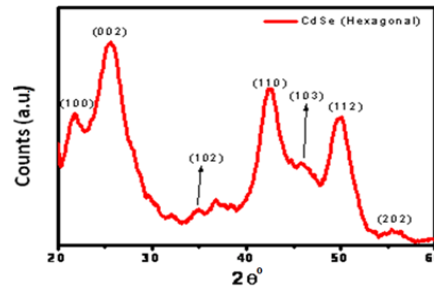


Figure 1: XRD Spectra of Prepared CdSe Nanocrystal

Table 1: The Calculated Particle Sizes and d-Spacing of CdSe Nanoparticle

2 θ of the Intense Peak (deg)	hkl	FWHM of Intense Peak (β) Radians	Size of the Particle (D) nm	d-Spacing nm
21.83	100	0.04	2.53	0.406
25.57	002	0.0505	2.82	0.348
34.89	102	0.0522	2.78	0.257
42.52	110	0.0358	4.15	0.212
45.86	103	0.0432	3.48	0.1977
49.97	112	0.047	3.55	0.182
55.75	202	0.071	2.21	0.164

UV-Visible Absorption Spectroscopic Data

Representative UV-vis absorption spectra for the prepared CdSe quantum dots samples are shown in figure 2. The peak positions of high sized CdSe nanoparticles are red shifted spectra compared to their corresponding small sized. This clearly indicates an increase in the nanoparticles diameter, as a result of the growth time. The diameter of the CdSe QDs for each growth time is estimated using the wavelength of the first excitonic absorption peak, (for wavelength ranging from 503 nm to 578 nm).

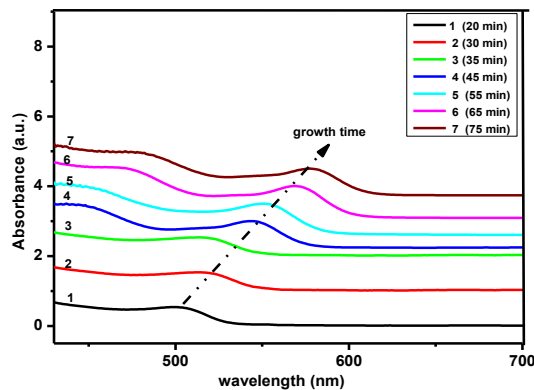


Figure 2: Optical Absorption Spectra of Selected Series of CdSe Nanocrystals: (1) 2.55 Nm, (2) 2.71 nm, (3) 2.75 nm, (4) 3.07 nm, (5) 3.25 nm, (6) 3.69 nm and (7) 3.86 nm

The sizes of the prepared CdSe samples are calculated from absorption *Yu's et al Method* [9], D (diameter/nm) = $(1.6122 \times 10^{-9}) \lambda^4 - (2.6575 \times 10^{-6}) \lambda^3 + (1.6242 \times 10^{-3}) \lambda^2 - (0.4277) \lambda + 41.75$. Where D (nm) is the size of a given nanocrystal sample and ' λ ' (nm) is the wavelength of the first excitonic absorption peak of the corresponding sample. The calculated sizes of our prepared samples corresponding to the λ_{\max} are shown in table 2. The sizing curve is depicted in figure 3.

Table 2: Calculated Size of the Prepared CdSe Nanocrystals Corresponding to λ_{\max} of the First Absorption Peak Using Yu *et al.* Equation

Samples No.	λ_{\max} of UV-vis Peak (nm)	NC Size D (nm)
1	503.55	2.55
2	518.70	2.71
3	521.14	2.75
4	542.30	3.07
5	551.53	3.25
6	569.92	3.69
7	577.92	3.86

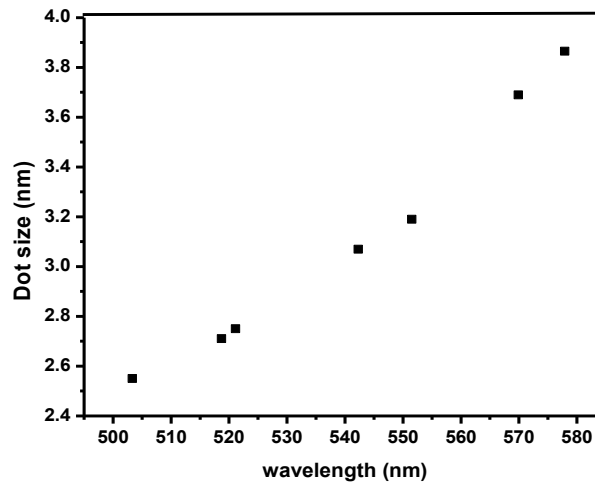


Figure 3: Absorption vs Size Relationship (Sizing Curve) for the Prepared CdSe Nanocrystals Calculated According to Yu *Et Al*

The optical band gap has been calculated from absorption coefficient data as a function of wavelength by using Tauc relation [10]. $(\alpha h\nu) = B (h\nu - E_g)^n$; where ' α ' is the absorption coefficient, ' $h\nu$ ' is the photon energy, 'B' is the band tailing parameter, ' E_g ' is the optical band gap of the nanoparticle, and ' n ' = 1/2 for direct band gap. The absorption coefficient (α), at the corresponding wavelengths, was calculated from Beer-Lambert's relation [11].

$$\alpha = \frac{2.3A}{d},$$

Where ' d ' is the path length and 'A' is the absorbance. It is well known that CdSe is a direct band gap semiconductor; hence the direct band gap value is estimated from the plots of $(\alpha h\nu)^2$ versus $h\nu$ is shown in figure 4 which is linear at the absorption edge, indicating a direct transition. The energy gap is determined by extrapolating the straight line portion to the energy axis at $(\alpha h\nu)^2 = 0$.

Table 3 summarized the energy gap (E_g) of CdSe nanoparticles. It is observed that the decrease of E_g values by the increasing of CdSe QDs size. The values of the band gap of CdSe nanoparticle are higher than the band gap of bulk. Whereas the bulk band gap value is 1.77 eV [12]. This is due to the strong quantum confinement. The direct band gap energies gradually increase from 2.12 eV

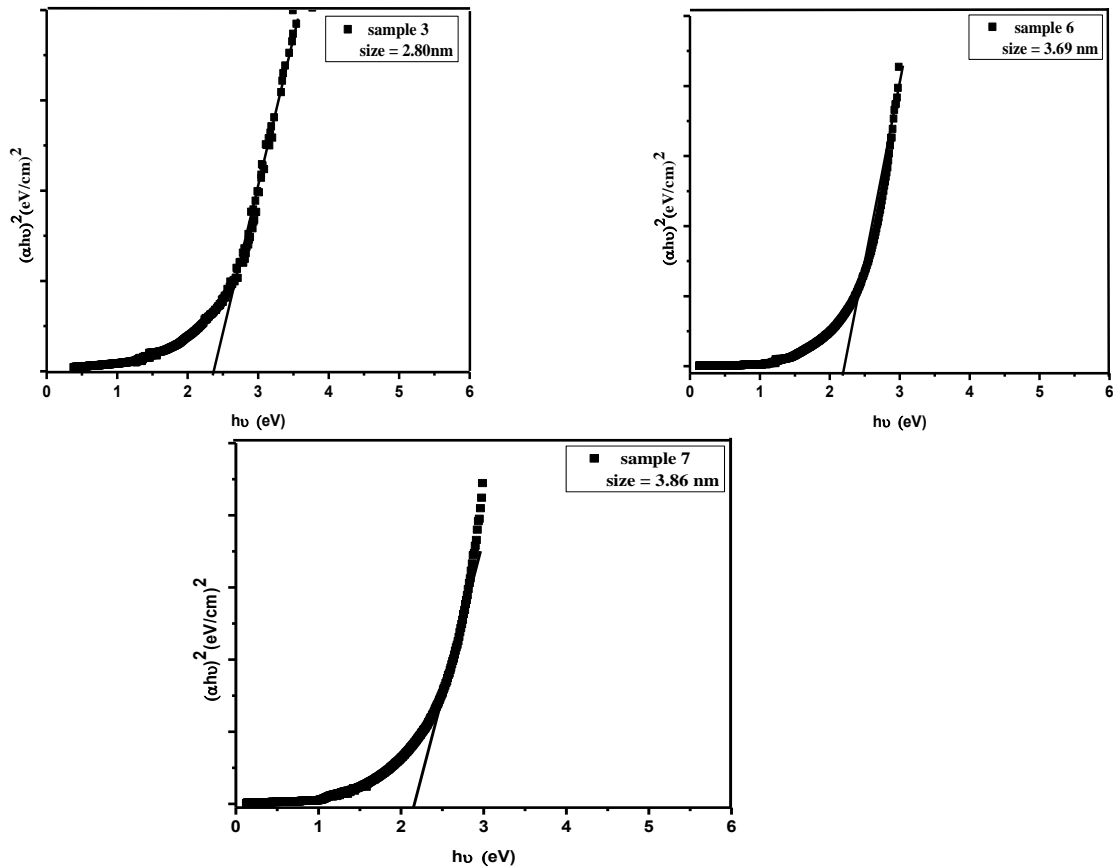


Figure 4: The Band Gap Determination, $(\alpha h\nu)^2$ vs $h\nu$ Plot of Prepared CdSe Nanoparticles at Different Sizes

Table 3: The Energy Gap (E_g) for CdSe Nanoparticles at Varies Sizes

Samples No.	E_g (eV)	NC Size (nm)
1	2.51	2.55
2	2.46	2.71
3	2.36	2.75
6	2.20	3.69
7	2.12	3.86

Fluorescence Spectroscopic of CdSe Nanoparticles

The Photoluminescence spectra of the prepared CdSe samples with varies sizes have been measured. Typical normalized photoluminescence spectra are shown in figure 5. The nanocrystals have maximum wavelength (λ_{\max}) in the fluorescence spectrum ranging between 525nm and 570nm. Importantly, the normalization allows for an easier comparison of peak emission and full width at half-maximum (FWHM) values. The FWHM of the photoluminescence spectra of CdSe NCs are all reasonably narrow and symmetric indicating a nearly monodispersed solution of NCs and no deep trap emission band in the red spectral region. The width values of the fluorescence spectra (FWHM) give information about the size distribution or monodispersity of the nanocrystals.

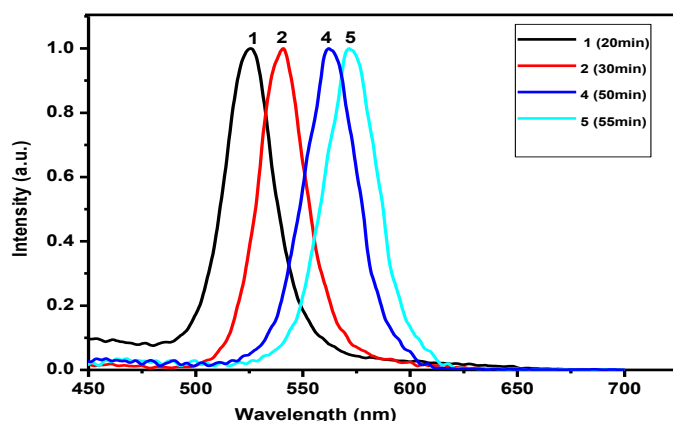
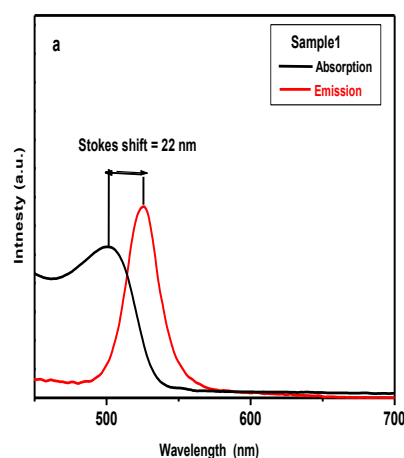
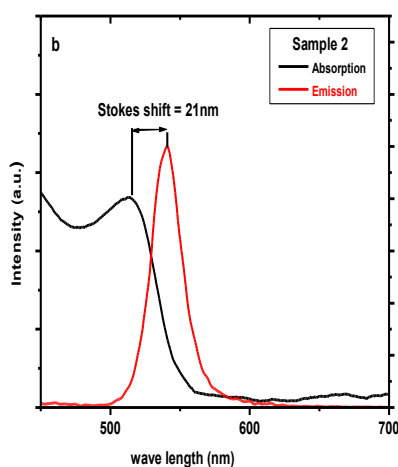


Figure 5: Photoluminescence (PL) Spectra of Prepared CdSe Nanoparticles: 1) 2.55 nm, 2) 2.71 nm, 4) 3.07 nm, 5) 3.25 nm. Intensities Obtained from a Fluorimeter were Normalized with Respect to the Maximum Value with *Origin lab v.7.5* Software

The absorption maxima occur at higher energies than the emission maxima as expected, the difference between the absorption and emission wavelengths is the Stokes shift. The prepared particle sizes have Stokes shifts of 22 nm, 21 nm, 20 nm and 19 nm for sample 1, 2, 4 and 5 respectively. These results are shown in table 4. Figure 6 shows the Stock shifts, which represent the energy difference between the absorption and emission for four prepared CdSe samples. It is clear that the Stock shift increases as the size decrease.

Table 4: Calculated Stock Shift of the Prepared CdSe Nanocrystals Corresponding to the Intensity of the Emission Spectra

Samples No.	λ_{\max} of abs. Spectra (nm)	λ_{\max} of emi. Spectra (nm)	Size, D (nm)	Stock Shift (nm)
1	503.55	525.50	2.55	22
2	518.74	540.06	2.71	21
4	542.3	562.30	3.07	20
	551.53	570.52	3.25	19



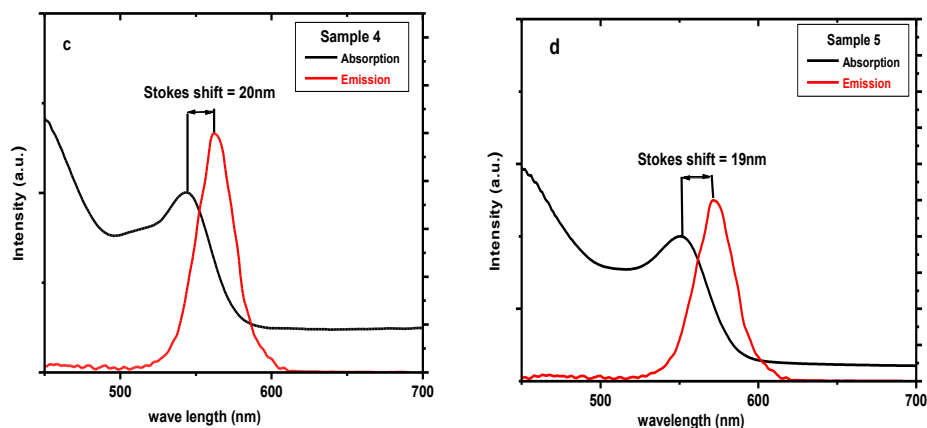


Figure 6: Stock Shift of the Fluorescence, Absorption (black line) and Emission (Red Line) of Four Prepared Samples of CdSe Nanocrystals (NCs) of Different Sizes, a) 20 Min, b) 30 Min, c) 45 Min, d) 55 Min

Transmission Electron Microscope (TEM) of CdSe Nanoparticles

The transmission electron micrograph results of CdSe nanoparticles and its particle size histogram for the micrograph are shown in figure 7. From the images one can see clearly a number of well-dispersed nanoparticles. The CdSe nanoparticles have an external spherical shape and the particles are to a large extent well-separated from one another and appear to be uniformly distributed throughout the field of the micrograph. The average particle size is ~ 4.2 nm, as shown in the histogram. The correlation between the size obtained from TEM and that obtained from the first excitonic transition in absorption spectrum provides reliable optical sizing of the nanocrystals. High-magnification imaging allows the detection of planar disorder in individual crystallites. The calculated d- spacing for the CdSe is found to be 0.190 nm which corresponding to the (103) plane, figure 7(d).

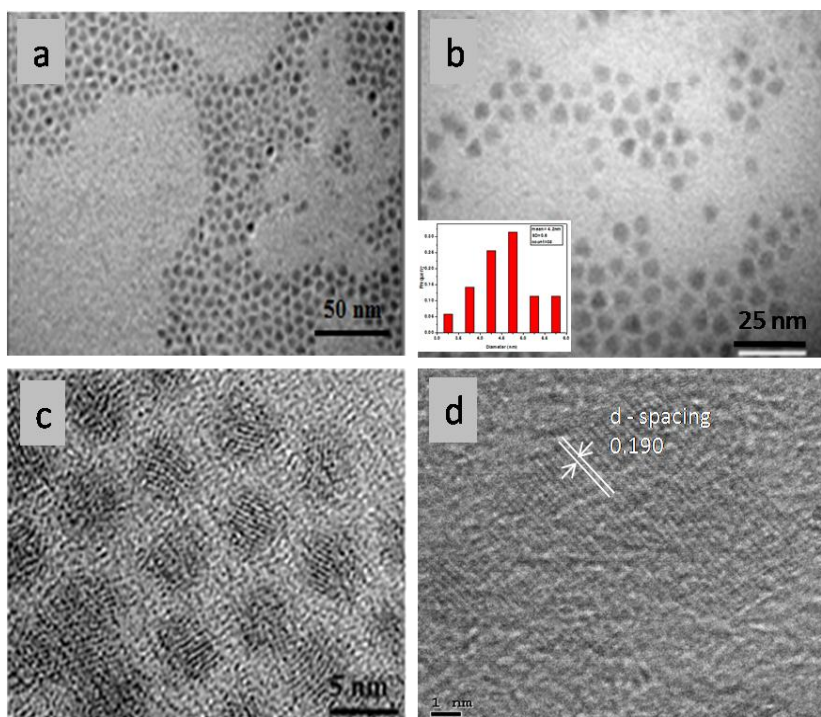


Figure 7: TEM Images of Selected CdSe Nanoparticle after Removal Time at 55min, ~ Size 4.2 nm

The particles size measured from TEM micrograph is larger than the value calculated from XRD data. This might be explained by the fact that, X-ray diffraction results based on the mean size of sample obtained from XRD patterns are smaller than that obtained from all the structural layers of sample when using TEM. Additional in XRD method we did not eliminate the system standard error. Mostly, the TEM images give more accurate size than that calculated using XRD data and absorption data.

CONCLUSIONS

Semiconductor nanocrystals have been prepared via organometallic pyrolysis method with some modification which is low cost and less hazardous. Analysis of the XRD patterns revealed that the formed phase of CdSe is wurtzite hexagonal structure. The CdSe nanoparticles were synthesized with an average particle size ranging from 2 nm to 4 nm. The average partial size measured from TEM micrograph is larger and more accurate than that of the value calculated from XRD. The band gap of CdSe samples increases with the decrease in the size of nanoparticles. This increase is outcome of quantum confinement effect originated from smaller size of nanoparticles for samples which are taken at lower temperature. The calculated band gaps of CdSe nanoparticles are higher than that of the bulk. Florescence measurements of CdSe QDs show a narrow emission with no sign of shallow trap or deep trap emission. From the FWHM of the emission band, it is clear that the CdSe samples are monodispersed and have small size distribution, The Stock shift of CdSe QDs increasing as the size of particles decreasing.

REFERENCES

1. Park, J. H.; Kim, J.Y.; Chin, B.D.; Kim, Y.C.; Park,O.O. (2004).White emission from polymer/quantum dot ternary nanocomposites by incomplete energy transfer *Nanotechnology* **15**, 1217.
2. Tansil, N.C. ; Gao, Z. (2006). Nanoparticles in biomolecular detection, *nts Nanotoday* **1** 28.
3. Colvin, V. L.; Schlamp, M. C. ; Alivisatos, A. P. (1994). Light emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer, *Nature* **370** 354-357.
4. YinY, Ling X.; Ge X.; Xia C.; Zhang Z. (1998). Synthesis of cadmium sulfide nanoparticles in situ using γ -radiation. *Chem Commun* **16**, 1641-1645.
5. Chan, W.C.W; Nie SM. (1998) Quantum dot bioconjugates for ultrasensitive nonisotopic detection.*Science*, **281**, 2016-2018.
6. Ma, C.; Ding, Y.; Moore, D.; Wang, X.; Wang, Z.L.(2004). Single-Crystal CdSe Nanosaws. *J Am. Chem. Soc.* **126** 708-711.
7. Murray, C.B.; Norris D.J.; and Bawendi M.G. (1993). Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **115**, 8706 -8715.
8. Cullity, B.D,(1956).Element of X-ray Diffraction, Addison-Wesley Company, USA.
9. Yu, W.W.; Qu, L.; Guo, W.; Peng, X. (2003) Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **15**, 2854 -2860.
10. Winter, J.O.; Gomez N.; Gatzert S.; Schmidt C.E.; Korge B.A. (2005). Variation of cadmium sulfide nanoparticle size and photoluminescence intensity with altered aqueous synthesis conditions. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **254**, 147-157.

11. Sahay P.P., Nath R.K., Tewari S. (2007). Optical properties of thermally evaporated CdS thin films. Cryst Res Technol **42**, 275-280.
12. Ethayaraja, M., C. Ravikumar, D. Muthukumaran, K. Dutta and R. Bandyopadhyaya, 2007. CdS-ZnS Core- Shell Nanoparticle Formation: Experiment, Mechanism, and Simulation. J. Phys. Chem., (C) **111** 3246-3252.

